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(54) Removal of organic cations from polar fluids.

(57) Cationic organic impurities such as ternary sulfonium ions and quaternary ammonium and phosphonium compounds are effectively removed from polar liquids such as water or water/alcohol mixtures by contacting the polar liquid with an absorbent comprising a trinitroarenol such as a picric acid. This method is particularly effective for removing such cationic impurities from polar liquids containing organic zwitterions.

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fonium chloride, triethylsulfonium chloride, bis(n-butyl)methylsulfonium bromide and analogs thereof. Examples of quaternary ammonium and phosphonium salts include tetramethylammonium bromide, benzyltrimethylammonium bromide, tetrabutylammonium bromide, trioctylmethylammonium chloride, triphenylmethylammonium bromide, tetraphenylphosphonium bromide and tetrabutylphosphonium chloride.

For the purposes of this invention, polar liquids are defined as normally liquid substances having a degree of polarity equal to or greater than that of octanol. Examples of suitable polar liquids include water, alkanols such as methanol and ethanol, ethylene glycol and monoethers of ethylene glycol and propylene glycol. Of these liquids, water is the most preferred.

In one preferred practice of the present invention, the polar liquid also contains an organic zwitterion which is not removed from the polar liquid during the practice of the improved method of this invention. Examples of such zwitterions are those described in U.S. Patents 4,089,877; 4,118,297; 4,130,543 and 4,111,914.

The absorbents employed in the practice of the invention contain a nitrated aromatic acid which is advantageously a trinitroarenol or a trinitroaryl sulfonic acid. By arenol is meant an aromatic compound having a phenolic hydroxyl. The trinitroarenols preferably employed include 2,4,6-trinitrophenol (picric acid) and 2,4-dinitrophenol, with picric acid being most preferred. Examples of preferred trinitroaryl sulfonic acids include 2,4,6-trinitrophenyl sulfonic acid and 2,4-dinitrophenyl sulfonic acid, with 2,4,6-trinitrophenyl sulfonic acid being most preferred.

In addition to the aforementioned acids, the absorbents also comprise a solid support or carrier such as activated carbon, alumina, titania or similar substrates, with activated carbon being most preferred. The solid support advantageously has an average particle diameter in the range from 0.08 to 2 millimeters (mm) and a surface area in the range from 900 to 1400 square meters/gram (N_2 BET method, ASTM D-3037). The activated carbon may also be bound to a suitable secondary support such as fibers of polyester or similar material.

The picric acid or other suitable nitrated aromatic acid is advantageously adsorbed on the support by exposing the support to a solution of the acid dissolved in water, alcohol or mixture thereof. This acid solution is preferably added to the top of a column of the absorbent and passed through the column such that the bottom portion of the column does not contain any of the acid.

In practicing the method of the invention, it is preferable to first prepare a cylindrical column of the absorbent of sufficient size to permit effective removal of the organic cation as well as an acceptable rate of flow of the polar liquid through the column. While the most optimum size of the column will vary with the particular organic cation to be removed, the particular polar liquid employed and the loading of acid on the support, the ratio of column length to diameter is preferably in the range from 1 to 10, with a ratio of 2.5:1 being most preferred.

The polar liquid is then passed through the cylindrical column at a rate in the range from 1 to 50 millimeters/minute per 11.4 square centimeters of column area, most preferably at a rate from 4 to 8 ml/min. per 11.4 cm^2. Normally the organic cation is removed under ambient conditions although somewhat higher than ambient pressures can be used to accelerate passage of the polar liquid through the column.

Upon the exit of the polar liquid from the column, the liquid, which usually contains less than 5 ppm, most preferably less than 0.5 ppm, of the organic cation, is ready for use or for further processing.

The following examples are given to illustrate the invention and should not be interpreted as limiting it in any way. Unless stated otherwise, all parts and percentages are given by weight.

Example 1

Sufficient activated carbon (20-50 mesh - ASTM-2862 obtained from Barneby-Cheney) is slurried in a 2-propanol/water mixture (20:80 by volume) and poured into a glass column (3.8 cm diameter) to yield a column which is 8.8 cm in length. The excess water/alcohol mixture is then eluted. A solution of 100 ml of 2-propanol/water (1:1 by volume) containing 0.5 gram of damp, purified 2,4,6-trinitrophenol (Picric Acid Purified, Sandoz Chemicals, Charlotte, N.C. 28205) is passed through the column at the rate of about 5 ml/min. After eluting the column with 100 ml of water, 450 grams of an aqueous solution of 44.1 grams of a bis(cyclic sulfonium aromatic) zwitterion represented by Formula I hereinafter and 0.044 gram of toxic cationic impurity represented by Formula II hereinafter are passed through the column at the rate of 5 ml/min. After eluting the column with 137 ml of water, 558.3 g of eluate containing 35.0 g of the zwitterion represented by Formula I is obtained. Analysis of the eluate using ion-exchange chromatography with gradient elution and photodiode-array detectors indicates that it contains less than 0.5 ppm based on zwitterion of the toxic cationic impurity.

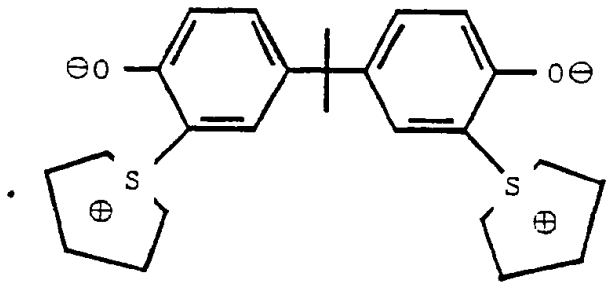
6. The improvement of Claim 5 wherein the quaternary ammonium ion is tetramethylammonium, benzyltrimethylammonium, tetrabutylammonium, trioctylmethylammonium or triphenylmethylammonium, and the quaternary phosphonium ion is tetraphenylphosphonium or tetrabutylphosphonium.

7. The improvement of Claim 2 wherein the polar liquid is water or a solution of water and an alkanol having up to 4 carbons which has dissolved therein an organic zwitterion.

8. The improvement of Claim 3 wherein the polar liquid is water or a solution of water and an alkanol having 2 or 3 carbons which has dissolved therein a cyclic aliphatic sulfonium zwitterion.

9. The improvement of Claim 7 or 8 wherein the zwitterion is represented by the formula:

Formula I



10. A method for removing cationic organic impurities from polar liquids which comprises the step of contacting a polar liquid containing a cationic organic impurity with an absorbent comprising a trinitroarenol or a trinitroaryl sulfonic acid under condi tions sufficient to remove substantially all of the impurity from the polar liquid.